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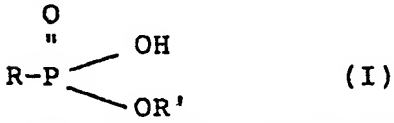
(71) Applicant: CIBA-GEIGY AG
Klybeckstrasse 141
CH-4002 Basel (CH)

(72) Inventor: Bentley, Robert Leonard, Dr.
34 Eddisbury Avenue
Urmston Manchester M31 2QJ (GB)

(54) Flame retardant polymer compositions.

(57) The present invention provides a composition comprising a halogen-free polymer and as a) flame retardant at least one metal or metalloid salt of a phosphonic acid of the general formula I



(I).

in which R is a straight or branched chain alkyl group having 1 to 3 carbon atoms optionally substituted by one or more halogen atoms or hydroxyl groups; and R' is H or an alkyl group having 1 to 3 carbon atoms and wherein the metal or metalloid is selected from Groups IIA, IIB, IIIA, IVA and VA of the "Periodic" Chart of Elements (Fisher Scientific Company c 1968) and b) a mono- or polycarboxylic acid or a metal or metalloid salt thereof, the metal or metalloid being selected from Groups I, IIA, IIB, IIIA, IVA and VA of the Periodic Chart of Elements (above).

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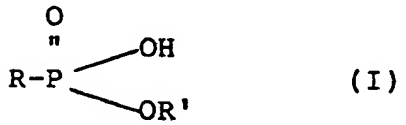
Description

Flame Retardant Polymer Compositions

The present invention relates to flame retardant polymer compositions containing phosphonic acid salts.

Polymers, particularly halogen-free polymers, are commonly made more flame retardant by incorporating therein a phosphorus-containing compound, a halogen-containing compound or a mixture thereof. Some polymers are processed at high temperatures of, for example, 250°C or higher, and many known flame retardants are not suitable under these conditions because they are too volatile, or not sufficiently thermally stable.

European Patent Application No. 0245207 describes and claims composition comprising a halogen-free polymer and a) as flame retardant at least one metal or metalloid salt of a phosphonic acid of the general formula I



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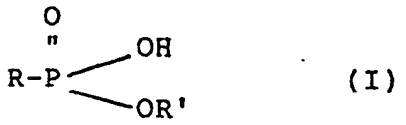
We have now found that the impact strength of these compositions is improved if a carboxylic acid or salt is incorporated as well as the phosphonic acid salts.

Accordingly the present invention provides a composition comprising a halogen-free polymer and a) as flame retardant at least one metal or metalloid salt of a phosphonic acid of the general formula I



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Halogen atoms in alkyl groups R, R' in I above are e.g. fluorine, bromine and chlorine atoms. The following are mentioned as haloalkyl groups R: chloromethyl, bromomethyl, trifluoromethyl, dichloromethyl, dibromomethyl, 2-chloroethyl, 1-chloropropyl and 1-bromopropyl. Alkyl groups R substituted by hydroxyl groups are preferably such groups substituted by one hydroxyl group such as, e.g. hydroxymethyl, 2-hydroxyethyl and 3-hydroxypropyl.

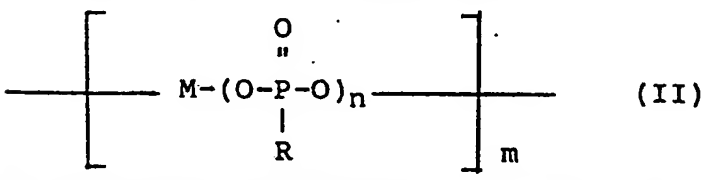
Preferably R represents unsubstituted C_1-C_3 alkyl but most preferably R is methyl.

R' is preferably hydrogen or methyl. The metal or metalloid in the phosphonic acid salt may be, for example, magnesium, calcium, barium, zinc, boron, aluminium, tin, or antimony. Preferably the metal is magnesium or aluminium, most preferably aluminium.

Particularly preferred are compositions wherein R and R' are each methyl and the metal is aluminium.

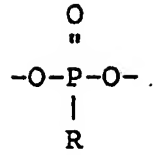
The salt may be a simple ionic compound formed between anions of the phosphonic acid and cations of the metal or metalloid.

Where R' is H and the metal of metalloid has a valency greater than one, the salt may have a polymeric structure as represented by the general formula II



(II)

where R is as defined above, M is the metal or metalloid, n has a value one less than the valency of M and m is from 2 to 100 and where each group



is attached to M atoms only.

If a monocarboxylic acid, or salt, is used, the acid may contain from 4 to 30 C atoms and may be a linear or branched alkyl, aralkyl or aryl carboxylic acid. Examples of such acids are butanoic, hexanoic, 2-ethylhexanoic, octanoic, decanoic, dodecanoic, stearic, phenylacetic, benzoic and naphthoic acids, especially stearic acid.

examples of polycarboxylic acid include succinic, maleic, adipic, pimelic, sebacic, phthalic acids, citric acid, pyromellitic acid and polycarboxylic acids prepared by polymerisation of one or more unsaturated mono- or di-carboxylic acids such as acrylic, methacrylic, maleic or itaconic acid or optionally by copolymerisation of one or more of these unsaturated carboxylic acids with an olefin such as ethylene, propylene, vinyl acetate or styrene.

Examples of these polycarboxylic acids include polyacrylic acid, polymaleic acid, copolymers of ethylene and acrylic acid and copolymers of maleic acid and styrene.

Where the carboxylic acids are used in the form of their metal or metalloid salts, suitable cations include lithium, magnesium, calcium, barium, zinc, boron, aluminium, tin or antimony.

When a metal or metalloid salt of a polycarboxylic acid is used, the carboxylic acid groups may be fully or only partially neutralised i.e. some free COOH groups may be present along with the COO^- groups.

The preferred carboxylic acid is a polycarboxylic acid, especially succinic, maleic, adipic, pimelic, sebacic or phthalic acid, or a polycarboxylic acid which is obtained by polymerisation of one or more unsaturated carboxylic acids with an olefin.

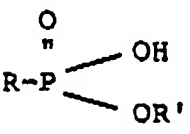
The amount of phosphonic acid salt added to the polymer as a flame retardant may be varied over a wide range. Usually from 0.1 to 100 parts by weight are used per 100 parts by weight of polymer. Preferably there are used 0.5 to 30 parts and, most preferably, from 2 to 20 parts by weight per 100 parts by weight of polymer. The optimum amount used depends on the nature of the polymer and the actual salt used and may be readily determined by simple experiment.

The phosphonic acids salts may be used in various physical forms depending on the polymer used and the desired properties. For instance the salts may be ground to a finely divided form to enable better dispersion throughout the polymer. Also mixtures of different salts may be used if desired.

The carboxylic acid or metal or metalloid salt can be used in an amount of from 1 to 10 parts, preferably 2 to 6 parts by weight based on 100 parts by weight or resin.

The carboxylic acid or salt can be added separately to the formulation along with the other ingredients prior to compounding or alternatively may be premixed with or coated onto the metal or metalloid salt of the phosphonic acid flame retardant or other ingredient of the formulation.

Accordingly the present invention also provides a composition comprising at least one metal or metalloid salt of a phosphonic acid of the general formula I



(I)

in which R is a straight or branched chain alkyl group having 1 to 3 carbon atoms optionally substituted by one or more halogen atoms or hydroxyl groups; and R' is H or an alkyl group having 1 to 3 carbon atoms and wherein the metal or metalloid is selected from Groups IIA, IIB, IIIA, IVA and VA of the "Periodic" Chart of Elements (Fisher Scientific Company c 1968) and a mono- or polycarboxylic acid or a metal or metalloid salt thereof, the metal or metalloid being selected from Groups I, IIA, IIB, IIIA, IVA and VA of the Periodic Chart of Elements (above).

Examples of polymers which may be rendered flame retardant are:

1. Polyphenylene oxides and sulfides, and blends of these polymers with polystyrene graft polymers or styrene copolymers such as high impact polystyrene, EPDM copolymers with rubbers, as well as blends or polyphenylene oxide with polyamides and polyesters.

2. Polyurethanes which are derived from polyethers, polyesters or polybutadiene with terminal hydroxyl groups on the one side and aliphatic, cycloaliphatic or aromatic polyisocyanates on the other side including polyisocyanurates, as well as precursors thereof.

3. Polyamides and copolyamides which are derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, such as polyamide 4, polyamide 6, polyamide 6/6, polyamide 6/10, polyamide 11, polyamide 12, poly-2,4,4-trimethylhexamethylene terephthalamide or poly-m-phenylene iso-phthalamide, as well as copolymers thereof with polyethers, such as for instance, with polyethylene glycol, polypropylene glycol or polytetramethylene glycols.

4. Polyesters which are derived from dicarboxylic acids and di-alcohols and/or from hydroxycarboxylic

acids or the corresponding lactones, such as polyethylene terephthalate, polybutylene terephthalate, poly,1,4-dimethylol-cyclohexane terephthalate and polyhydroxybenzoates as well as block-copolyether-esters derived from polyethers having hydroxyl end groups.

5. Unsaturated polyester resins which are delved from copolyesters or saturated and unsaturated dicarboxylic acids with polyhydric alcohols and vinyl compounds as cross-linking agents.

6. Polystyrene.

7. Graft copolymers of styrene, such as, for example, styrene on polybutadiene, styrene and acrylonitrile on polybutadiene, styrene and alkyl acrylates or methacrylates on polybutadiene, styrene and acrylonitrile on polyacrylates or polymethacrylates, styrene and acrylonitrile or acrylate/butadiene copolymes, as well as mixtures thereof with random copolymers of styrene or α-methylstyrene with dienes or acrylic derivatives, for instance the terpolymers of styrene known as ABS, MBS, ASA or AES terpolymers.

8. Cross-linked epoxide resins which are derived from polyepoxides, for example, from bis-glycidyl ethers, especially bisphenol A diglycidyl ethers, or from cycloaliphatic diepoxides.

9. Polycarbonates.

The polymer is preferably a polyphenylene oxide or sulphide, or a blend thereof with a polystyrene graft polymer or a styrene copolymer.

The compositions of the invention may also contain other conventional ingredients, such as heat stabilisers, light stabilisers, ultra-violet light absorbers. anti-oxidants, anti-static agents, preservatives, adhesion promoters, fillers, pigments, lubricants, blowing agents, fungicides, plasticisers, processing aids, other fire-retardant additives and smoke suppressants.

Other fire retardant additives which may be used with the phosphonic acid salts include phosphorus containing esters and salts such as triaryl phosphates, alkyl aryl phosphates and ammonium polyphosphate, halogen, especially bromine- and chlorine-containing compounds such as decabromo diphenyl ether, hexachlorocyclopentadiene, brominated polystyrene, haloalkyl phosphate and phosphonate esters, antimony oxide, hydrated alumina, bismuth oxide, molybdenum oxide, or mixtures of these compounds with zinc and/or magnesium oxide or salts.

The invention is illustrated by the following Examples.

Examples 1 to 5

Compositions are made comprising a polymer blend of polyphenylene oxide (PPO) and high impact polystyrene (HIPS), and aluminium methyl methylphosphonate.

The ingredients are dry blended in a high-speed blender and extruded using a Baker-Perkins twin screw extruder. The resulting polymer is compression moulded to give plaques which are cut into test pieces. The Izod impact strength is determined according to the method given in ASTM D256.

The improvement in impact strength obtained by incorporation of the carboxylic acids or salts thereof is shown by reference to Examples 2 to 5 compared to Example 1 which is a formulation without the impact strength improvement additives.

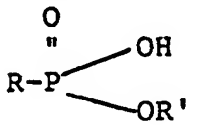
Formulation parts by wt.	Example No.				
	1	2	3	4	5
PPO [1]	35	35	35	35	35
HIPS [2]	65	65	65	65	65
Aluminium Methyl [3] Methylphosphonate	10	10	10	10	10
Irganox ® 1010 [4]	0.2	0.2	0.2	0.2	0.2
Stearic Acid	-	2	-	-	-
Calcium stearate	-	-	3	-	-
Zinc stearate	-	-	-	3	-
ACLYN ® 295A [5]	-	-	-	-	3
Notched Izod Impact strength (J m^{-1})	82	96	124	99	96

Notes:

1. Polyphenylene oxide
2. High impact grade of polystyrene
3. Prepared according to method in European Patent Application 0245207
4. Stabiliser, Trade mark of Ciba-Geigy AG
5. Zinc salt of ethylene/acrylic acid copolymer supplied by Allied Corporation International SA

Claims

1. The present invention provides a composition comprising a halogen-free polymer and as a) flame retardant at least one metal or metalloic salt of a phosphonic acid of the general formula I



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2. A composition as claimed in claim 1 in which R represents unsubstituted C_1-C_3 alkyl.

3. A composition as claimed in claim 2 in which R represents methyl.

4. A composition as claimed in claim 1 in which R' represents hydrogen or methyl.

5. A composition as claimed in claim 1 in which the metal of metalloid in the phosphonic acid salt is magnesium, calcium, barium, zinc, boron, aluminium, tin or antimony.

6. A composition as claimed in claim 1 in which R and R' are both methyl and the metal is aluminium.

7. A composition as claimed in claim 1 in which the carboxylic acid is a monocarboxylic acid having 4 to 30 C atoms and is linear or branched alkyl, aralkyl or aryl carboxylic acid.

8. A composition as claimed in claim 7 in which the carboxylic acid is butanoic, hexanoic, 2-ethylhexanoic, octanoic, decanoic, dodecanoic, stearic, phenylacetic, benzoic or naphthoic acid.

9. A composition as claimed in claim 1 in which the carboxylic acid is a polycarboxylic acid.

10. A composition as claimed in claim 9 in which the polycarboxylic acid is succinic, maleic, adipic, pimelic, sebacic or phthalic acid.

11. A composition as claimed in claim 9 in which the polycarboxylic acid is one obtained by polymerisation of one or more unsaturated mono- or di-carboxylic acids or by copolymerisation of one or more unsaturated carboxylic acids with an olefin.

12. A composition as claimed in claim 11 in which the polycarboxylic acid is polyacrylic acid, polymaleic acid, a copolymer of ethylene and acrylic acid or a copolymer of maleic acid and styrene.

13. A composition as claimed in claim 1 in which the carboxylic acid is in the form of a salt with lithium, magnesium, calcium, barium, zinc, boron, aluminium, tin or antimony.

14. A composition as claimed in any preceding claim in which the amount of phosphonic acid salt is from 0.1 to 100 parts by weight per 100 parts by weight of polymer.

15. A composition as claimed in claim 14 in which the amount of salt is from 0.5 to 30 parts by weight per 100 parts by weight of polymer.

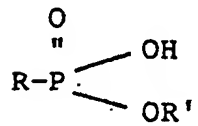
16. A composition as claimed in claim 15 in which the amount of salt is from 2 to 20 parts by weight per 100 parts by weight of polymer.

17. A composition as claimed in claim 1 in which the amount of carboxylic acid or salt thereof is from 1 to 10 parts by weight per 100 parts by weight of polymer.

18. A composition as claimed in claim 17 in which the amount of carboxylic acid or salt thereof is from 2 to 6 parts by weight per 100 parts by weight of polymer.

19. A composition as claimed in claim 1, in which the polymer is a polyphenylene oxide or sulphide, or a blend thereof with a polystyrene graft polymer or a styrene copolymer.

20. A composition comprising at least one metal or metalloid salt of a phosphonic acid of the general formula I



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EUROPEAN SEARCH REPORT

Application Number

EP 89 81 0345

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A,D	EP-A-0 245 207 (CIBA-GEIGY AG) * Claims * -----	1	C 08 K 5/00 C 08 L 101/00 // (C 08 K 5/00 C 08 K 5:04 C 08 K 5:53)

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 08 K
C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-08-1989	HOFFMANN K.W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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